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MAX-DOAS detection of glyoxal during ICARTT 2004

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Abstract

The direct detection of glyoxal (CHOCHO), the smallest α-dicarbonyl, in the open atmosphere by active differential optical absorption spectroscopy (DOAS) has recently been demonstrated (Volkamer et al., 2005a) and triggered the very recent successful detection of CHOCHO from space (Kurosu et al., 2005; Wittrock et al., 2006; Beirle et al., 2006). Here we report the first detection of CHOCHO by passive multi axis differential optical absorption spectroscopy (MAX-DOAS). CHOCHO and NO_2 slant column measurements were conducted at MIT, Cambridge, USA, and on board the research vessel Ron Brown in the Gulf of Maine as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) 2004 campaign. For a day with nearly clear sky conditions, radiative transfer modeling was employed to derive diurnal CHOCHO mixing ratios for both sites. CHOCHO mixing ratios at MIT varied from 40 to 120 ppt, with peak values observed around noon. Mixing ratios over the Gulf of Maine were found to be up to 3 times larger than at MIT. The CHOCHO-to-NO_2 ratio at MIT was <0.03, and enhancements of this ratio by up to two orders of magnitude were found over the Gulf of Maine. This paper focuses on the instrumental aspects involved with MAX-DOAS measurements of CHOCHO.

1 Introduction

Glyoxal (CHOCHO) is the smallest α-dicarbonyl and is an oxidation product of numerous volatile organic compounds (VOCs) (Calvert et al., 2000; Volkamer et al., 2001; Calvert et al., 2002). Direct and time resolved CHOCHO measurements provide a useful novel indicator to constrain VOC oxidation processes (Volkamer et al., 2005a), and enable many useful applications, such as an improved source apportionment of formaldehyde (HCHO) in urban air (Garcia et al., 2005). The atmospheric residence time of CHOCHO is limited by rapid photolysis and reaction with OH radicals, and is about 1.3 h for overhead sun conditions (Volkamer et al., 2005a). An increasing body

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of evidence recently suggests that volatile CHOCHO possibly contributes to secondary organic aerosol (SOA) formation (Liggio et al., 2005; Kroll et al., 2005; Volkamer et al., 2006). However, the atmospheric relevance of CHOCHO uptake on aerosols is presently not clear.

The strongest absorption bands of CHOCHO are located in the blue wavelength range between 420 and 460 nm (Volkamer et al., 2005b). These bands have recently been used to measure CHOCHO for the first time directly in the open atmosphere, as part of the MCMA 2003 campaign in Mexico City, using an active differential optical absorption spectroscopy (DOAS) device (i.e. using a Xe-arc light source). It has further been suggested that the detection of CHOCHO by passive DOAS, i.e. using scattered sunlight as a light source, should be feasible from ground- or space-borne platforms (Volkamer et al., 2005a). Most recently measurements of CHOCHO from space have been accomplished by three research teams using two satellite platforms (i.e. OMI and SCIAMACHY) (Kurosu et al., 2005; Wittrock et al., 2006; Beirle et al., 2006). In this study we follow up on (Sinreich et al., 2004) and present the first observation of CHOCHO using passive ground-based DOAS instrumentation.

DOAS is a well established technique for the detection of trace gases in the atmosphere (Platt, 1994). The position and optical density of narrow band absorption features (<5 nm width) in the light spectra are analyzed to selectively detect and quantify trace gases by applying the Lambert-Beer's law. Like most spectroscopic techniques DOAS is inherently self-calibrating as well as contact free, it identifies the particular molecules unequivocally by their characteristic absorption structure (see Fig. 1), and allows real time measurements (Platt 1999). The DOAS technique allows to measure numerous trace gases like e.g. NO_2, O_3, SO_2, HCHO, NO_3, BrO, OClO and – as discussed in this article – CHOCHO. In contrast to active DOAS instruments, where artificial light sources are employed, passive DOAS devices use natural light sources like the sun. Measurements of scattered sunlight can be performed with a relatively simple setup and very low power consumption (Solomon et al., 1987; Otten et al., 1998; Bobrowski et al., 2003; Galle et al. 2003). “Traditional” setups point only to the zenith and are mostly sensitive to trace gases located in the stratosphere. To increase the sensitivity to trace gases close to the surface, the Multi-Axis-DOAS (MAX-DOAS) technique has been developed recently. MAX-DOAS instruments observe scattered sunlight from a variety of viewing directions. In particular, high sensitivity for gases close to the ground is obtained for observation directions pointing slightly above the horizon (Hönninger and Platt, 2002; Leser et al., 2003; van Roozendael et al., 2003; Wittrock et al., 2004; Hönninger et al., 2004; Wagner et al, 2004; Heckel et al., 2005; von Friedeburg et al., 2005; Frieß et al., 2006). Furthermore, some degree of vertical resolution can be obtained by measuring along different lines of sight. In particular, when assuming a well mixed trace gas layer (e.g. within the atmospheric boundary layer), its vertical extent can be determined with good accuracy (e.g. Hönninger and Platt, 2002, Sinreich et al., 2005; Frieß et al., 2006) which generally is not possible with active DOAS devices.

The primary quantity of a DOAS measurement is the "slant column density" (SCD), which is the integrated concentration over the light path, or more realistically the average integrated concentration over many possible light paths. In contrast, the "vertical column density" (VCD) is the integrated concentration over a vertical path through the atmosphere. Thus, the VCD is independent of the particular measurement geometry and the sunlight conditions. The ratio between SCD and VCD defines the air mass factor (AMF), which expresses the light path extension compared to the vertical path through the atmosphere. Because of the complexity of radiative transfer, AMFs are usually calculated using numerical radiative transfer models (Solomon et al., 1987; Marquard et al., 2000). The calculated AMFs can be used for inverse modeling which means that the parameters of the calculations are altered until the model output matches the measured SCDs. In this study, we derive height information from MAX-DOAS measurements on aerosol extinction as well as on mixing ratios of CHOCHO.

Our MAX-DOAS observations were part of the ICARTT 2004 campaign, which took place from 1 July through 15 August 2004. A network of 6 passive DOAS devices was set up in the north-eastern USA: at Thompson Farm (University of New Hampshire), in

Cambridge (Massachusetts Institute of Technology (MIT)), at Harvard Forest (Harvard University), in Narragansett (University of Rhode Island), at Brookhaven National Lab and at Pinnacle State Park (University of Albany). Additionally, a MAX-DOAS device was set up on the research vessel Ron Brown which cruised through the Gulf of Maine during the measurement period. These MAX-DOAS devices were used to measure NO_2, SO_2, HCHO and O_4. Two of them also measured CHOCHO.

2 Measurement sites and instruments

The two MAX-DOAS instruments with the capability to detect CHOCHO (owing to the selected wavelength range of the spectrographs) were those at MIT and RV Ron Brown. The first instrument was located on one of the buildings (Building 54, the so-called Green Building) of the MIT in Cambridge at 42.36° northern latitude and 71.09° westerly longitude; the instrument was pointing to the north. The second instrument was installed on the research vessel Ron Brown during its cruise in the Gulf of Maine, looking starboard. In this case, the observation azimuth varied depending on the course of the vessel.

At MIT a “Mini-MAX-DOAS” device (Bobrowski, 2004) was operated. It contained a miniature crossed Czerny-Turner spectrometer/detector unit “USB2000” from Ocean Optics Inc. with a resolution of 0.7 nm FWHM, projecting the spectral range from about 330 to 462 nm onto a one-dimensional CCD-detector with 2048 pixels. The spectrometer/detector unit was cooled to a stable temperature of +15°C which at the same time minimized changes in optical properties of the spectrometer while reducing detector dark current. The sunlight was collected and focused by a quartz lens and was lead into the spectrograph/detector unit by a quartz fibre bundle. To avoid condensation of water vapour, the instrument was sealed and a drying agent was included. An attached stepper motor enables the adjustment of the viewing direction to a desired elevation angle (“elevation” is defined as the angle between the horizon and the pointing direction of the telescope). All functions were controlled by PC via USB connection.

The MAX-DOAS instrument installed on the RV Ron Brown consisted of three small telescopes which simultaneously collected scattered sunlight from different elevation angles (Wagner et al., 2004). Each of them could be individually adjusted by stepper motors to any elevation angle between horizon and zenith. In order to prevent influences on the telescope viewing directions caused by rolling and pitching of the vessel, the telescopes were mounted on a Cardanic suspension which largely compensated for these movements. The sunlight was focused on quartz fibre bundles using quartz lenses before it reached the spectrometer, a commercial instrument with 300 mm focal length (Acton model 300). The spectra were detected by a two-dimensional imaging CCD-detector (Andor model DV420-OE). While the spectrometer was heated to a stable temperature of +32°C, the CCD-detector was cooled to –30°C for the reasons already described above. The signals originating from the three telescopes reached the two-dimensional detector at well defined different areas which allowed them to be clearly separated afterwards. The spectrometer covered the wavelength range from 325 to 460 nm and had a resolution of about 0.7 nm FWHM.

Both setups were operated by fully automated measurement routines – Doasis (DOAS Intelligent System) (Kraus, 2001) at MIT and a specialized measurement program (Frieß, 2001) on the RV Ron Brown. Both programs employed routines to adapt the integration time of the measurements to the light conditions in order to achieve a constant signal level (i.e. constant signal maximum per exposure), to store the spectra and to control the pointing of the telescopes. The instrument slit functions were determined by measuring the emission line of a mercury lamp at 436 nm.

The telescopes were moved sequentially after each measurement, and scattered light spectra were acquired at elevation angles of 3°, 6°, 10°, 18° and from the zenith (the field of view of the telescopes is about 1°). A sequence of the five elevation angles was completed after approximately 5–15 min.

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3 The DOAS analysis

The CHOCHO SCDs were derived from the recorded spectra by an analysis procedure using the Windoas software package (Fayt and van Roozendael, 2001) from IASB (Belgium Institute for Space Aeronomy). To the logarithm of the measured spectrum, several trace gas cross sections as well as the logarithm of a Fraunhofer reference spectrum (FRS), a Ring spectrum (Grainger and Ring, 1962; Bussemer, 1993) and a polynomial of degree 5 are fitted based on a non-linear least squares fitting algorithm. The zenith spectrum from the previous measurement sequence (see above) was chosen as FRS so that it was updated from sequence to sequence. This procedure leads to minimal influence of instrumental instabilities and largely to an elimination of the stratospheric contribution to the SCD. The Ring spectrum and the polynomial correct for Raman scattering as well as Rayleigh and Aerosol scattering, respectively. The Ring spectrum was calculated from the according FRS for each sequence and thus changed from sequence to sequence, too. Also, included in the fitting routine was an intensity offset (polynomial of degree 1) to account for possible instrumental stray light. The measurement spectrum was allowed to be shifted against the FRS, the Ring spectrum and the cross sections (Stutz and Platt, 1996). The wavelength calibration was performed using the Doasis software by fitting the Fraunhofer reference spectra to a high resolution Fraunhofer spectrum (Kurucz et al., 1984) convoluted by the instrument's slit function (see above).

The following high resolution absorption cross sections were included in the retrieval: CHOCHO (Volkamer et al., 2005b), NO_2 (Vandaele et al., 1997), ozone at 223 K (Bogumil et al., 1999) and O_4 (Greenblatt et al., 1990). These cross sections were convoluted with the instrumental slit function to match the spectral resolution of the instruments (except the O_4 spectrum which was interpolated). In addition, we used a water vapor reference spectrum derived from our own atmospheric measurements. This was done because the literature water vapor cross sections are still of poor quality, especially in the wavelength range used in our retrievals. The measured water vapor reference

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spectrum was derived from the ratio of two spectra (Heintz 1996), one with high (at 3° elevation) and one with low water vapor absorption (at zenith direction). In order to minimize the potential interference with CHOCHO absorption we restricted our measured water vapor reference spectra to the wavelength range of the actual water vapor absorption (from 438.5 to 454 nm). For the MIT instrument, the morning of 17 July 2004, when the humidity was high, was selected. The same was done for the RV Ron Brown by using observations performed on 6 July 2004, also a day with water vapor amounts above the average. The water vapor measurement was taken at about 07:00 a.m. and 06:00 a.m., respectively, when the least amount of CHOCHO is expected to be present in the atmosphere. Since the water vapor reference spectra were derived by the instruments themselves, their specific optical properties are inherently leading to a better spectral retrieval with less systematic structures. For the CHOCHO evaluation, the spectral range from 420 to 460 nm was chosen (458 nm on the RV Ron Brown due to the restricted spectral range of the instrument), encompassing three main CHOCHO absorption bands.

While the SCDs of NO_2 were retrieved together with CHOCHO, O_4 was analyzed in the wavelength range between 338 and 364 nm encompassing two absorption bands. Cross sections of O_4 (Greenblatt et al., 1990), NO_2 (Vandaele et al., 1997), BrO (Wilmouth et al., 1999), HCHO (Meller and Moortgat, 2000) and of O_3 (Bogumil et al., 1999) at two temperatures (243 K and 223 K) were fitted. Furthermore, a Ring spectrum, a polynomial of degree 3 and an intensity offset of degree 2 were included into the fit.

Typically, NO_2 is the dominant absorber in the retrieval and its absorption cross section shows characteristic structures. Thus, even small potential errors in the analysis of the NO_2 absorption (e.g. due to the temperature dependence of the cross section or due to an inaccurate wavelength calibration) might substantially affect the retrieved CHOCHO results. In this case, the CHOCHO-to-NO_2 ratio should provide an indication of a potential interference with NO_2. Since the CHOCHO-to-NO_2 ratio shows a variable behavior for each elevation angle and for both sites (for 3° elevation angle see Fig. 5)

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such an interference could be clearly excluded.

Furthermore, several sensitivity studies were performed in order to quantify any systematic error in the CHOCHO retrieval. We varied the wavelength range and the degree of the polynomial as well as of the intensity offset. Furthermore, we used a water vapor cross section from literature (Rothman et al., 1998) instead of our measured water vapor reference spectrum. While the residual structures were significantly larger, the results for CHOCHO were almost the same as for our original settings. This indicates that our retrieved water vapor reference indeed does not contain significant absorption structures of CHOCHO. Finally, for the measurements at MIT we also used a measured NO_2 reference spectrum instead of the cross section taken from literature (for the RV Ron Brown no measured NO_2 spectrum was available). It was measured in the early afternoon of 12 July 2004, a slightly misty, but sunny day with constant lighting conditions, from two zenith spectra one with and one without NO_2 cell in the field of view. For the described sensitivity studies the results for CHOCHO were robust within ±15%.

4 Profile inversion

In the following, we give a short overview on the inversion procedure (Sinreich et al., 2005) employed to convert the measured SCDs into aerosol optical densities (AODs) and trace gas mixing ratios. In a first step, this procedure exploits the fact that the concentration of O_4 is proportional to the square of the O_2 concentration, which has only a small spatial and temporal variability caused by pressure and temperature changes. Variations of the O_4 SCDs thus mainly reflect changes in the optical properties of the atmosphere. Therefore, O_4 delivers information on the light paths through the atmosphere and can be considered as a good indicator for the aerosol load (Wagner et al., 2004; Frieß et al., 2006). O_4 AMFs were simulated for various aerosol scenarios using the radiative transfer model "Tracy" (von Friedeburg, 2003) and compared to the measured O_4 AMFs, obtained by dividing the O_4 SCDs by a typical O_4 VCD. For the

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simulation, the aerosols were assumed to be homogeneously mixed in the planetary boundary layer (PBL), and the mixing height H and aerosol extinction coefficient $\varepsilon_{\text{Aerosol}}$ were varied. The (H, $\varepsilon_{\text{Aerosol}}$) pair (the product of which is the AOD) that best represented the O_4 SCD measurements was then used to calculate AMFs for CHOCHO. The concentrations of the trace gases also were assumed to be constant in the PBL. The comparison of the ratio between the 3° and the 18° values of the modeled AMFs and of the measured SCDs yields H, which allows deriving the mixing ratio. Owing to the strong dependence of measured SCDs on the elevation angle, such a profile inversion in principle can be done for each sequence of elevation angles. In this study, we applied the profile inversion for observations averaged over about one hour. This reduces atmospheric variations as well as measurement noise of single observations. The comparisons were performed for solar zenith angles of 25°, 30°, 40°, 60° as well as 70° (MIT) and 75° (RV Ron Brown), respectively.

5 Results and discussion

Elevated concentrations of CHOCHO were detected at MIT in Cambridge and onboard RV Ron Brown on more than 10 days during the measurement period. The SCDs are generally significantly lower at MIT than onboard RV Ron Brown.

An example for the retrieval of CHOCHO from the instrument onboard the RV Ron Brown is shown in Fig. 1. The spectrum was taken under sunny conditions on 10 July 2004, at about 05:15 pm at an elevation angle of 3°. At this time, the vessel was cruising along the coast of Massachusetts (42.09° N, 70.59° W) with wind from westward directions. The optical densities of the fitted components as a function of wavelength are shown in black, whereas the red lines show the sum of the scaled cross-sections and the residual. The root mean square variation of the residual (Fig. 1f) in this evaluation is 0.34×10^{-3} which is less than one tenth of the retrieved optical density of CHOCHO (approx. 3.5×10^{-3}) and therefore is clearly low enough to allow an unequivocal detection of CHOCHO (Stutz and Platt, 1996). The corresponding

SCD amounts to 6.74×10^{15} molec/cm^2 at a 1σ error of 3.00×10^{14}. The SCDs of NO_2 (3.55×10^{16} molec/cm^2), water vapor, O_4 and O_3 are also clearly identified.

In Fig. 2, measured tropospheric SCDs of CHOCHO, NO_2 and O_4 are plotted for both sites, each on a clear day, which can be identified by a relatively smooth variation of the O_4 SCDs during the day. At MIT, the chosen day is 26 July, which showed an increase in the CHOCHO SCDs (Fig. 2a) up to about 3.5×10^{15} molec/cm^2 in the morning, indicating a very efficient VOC oxidation on that day. In the afternoon, the values decreased again most probably caused by chemical loss. A concentration reduction caused by dilution in a rising PBL would hardly affect the CHOCHO SCDs since MAX-DOAS measurements integrate the absorptions signal over the height. The described behavior of the CHOCHO SCDs is consistent with active DOAS observations in Mexico City (Volkamer et al., 2005a). The NO_2 SCDs do not show such a pronounced diurnal cycle, although a decrease in the afternoon is also observable. The diurnal variation of the NO_2 values appears to be rather dominated by the light path distribution, as can be seen from the similarity to the variation in the O_4 SCDs. 17 July was a clear day for the RV Ron Brown. On this day, the vessel cruised around 69° W and 43° N in the Gulf of Maine mainly in eastward direction, at about the same latitude as Portsmouth, New Hampshire. The wind came from southwest to west during the day. Here the CHOCHO SCDs (Fig. 2d) are more influenced by the light path variations whereas the NO_2 SCDs show high tropospheric NO_2 in the morning which disappeared in the afternoon. In the late afternoon, the course of the vessel changed to northwest and a new and slightly cleaner air mass seemed to be present. For both days, radiative transfer modeling was performed to convert SCDs into mixing ratios. For these calculations, an O_4 cross section value of 5×10^{46} cm^5/molec^2 (for the 361 nm absorption band) was assumed (for the definition of the O_4 cross section see Greenblatt et al., 1990).

In Fig. 3, the estimated profile heights H and AODs are shown for both sites. The aerosol and CHOCHO profile heights at MIT generally match well, except for some deviations in the morning and evening, when CHOCHO SCDs were lowest. During mid-day, the signal to noise ratio of the SCDs is highest and the radiative transfer modeling is more accurate. At RV Ron Brown, the modeling of the aerosol layer height did not lead to an unequivocal result due to the relatively high AOD. The AOD at MIT increased in the course of the day which indicates an accumulation of aerosol load during that day. At RV Ron Brown, an accumulation can also be observed whereas a sudden decrease in the late afternoon indicates an altered air mass as already seen in SCDs.

The resulting CHOCHO mixing ratios at MIT (Fig. 4a) have their maximum at noon with about 120±30 ppt (1 ppt=1 part per trillion=2.51×10^7 molec/cm^3 at 293 K and 1013 mbar). In contrast, there is no such clear maximum on RV Ron Brown (Fig. 4b) and the maximum values are almost three times higher (up to 340±110 ppt). In the MCMA-2003 campaign, values up to 1.82 ppb (1 ppb=1 part per billion=1000 ppt) were measured (Volkamer et al., 2005a). Typical daytime maxima were about five times larger in Mexico City than in Cambridge.

Figure 5 shows the CHOCHO-to-NO_2 SCD ratio at 3° elevation for the chosen days for the MIT site (Fig. 5a) and the RV Ron Brown (Fig. 5b). At MIT, the ratio reached its maximum (0.028±0.008) at 01:30 p.m., a much smaller value than observed during MCMA-2003 where daily maximum ratios varied between 0.045 and 0.14 (Volkamer et al., 2005a). The MCMA-2003 campaign average ratio (0.081) is two to three times higher than in Cambridge, possibly reflecting differences in the VOC/NO_x ratio (NO_x = NO + NO_2) between both urban sites. The ratio also peaked earlier in Mexico City than in Cambridge, reflecting more active and earlier PBL dynamics in Mexico City (de Foy et al., 2005) than in Cambridge. In contrast, the ratios onboard RV Ron Brown were much higher and peaked even later in the day. On 17 July 2004, the ratio reached up to 3.1±0.9 at 03:00 p.m. This is 110±45 times higher than at MIT.

The considerably higher CHOCHO-to-NO_2 ratio over the sea compared to the Cambridge values can partly be explained by the fact that CHOCHO is a secondary pollutant, i.e. formed from the airborne VOC oxidation, in contrast to NO_2 from NO_x emissions. Sustained CHOCHO formation from longer lived VOC precursor oxidation in combination with NO_x removal in the photochemical plume will thus lead to higher

CHOCHO-to-NO_2 ratios downwind of emission sources. For a rough estimation of the extent of the NO_2 removal effect, we assume that the air mass needed half a day to reach the RV Ron Brown from the last emission source (with a distance of about 200 km and a wind speed of about 5 m/s), and that the air mass contained an OH concentration of about 2.6×10^6 molecules per cm^3. This number is the retrieved 24 h average OH concentration during NEAQS-2002 for air masses that had been impacted by major urban areas such as New York City and Boston and by biogenic emissions in New Hampshire and Maine (Warneke et al., 2004). Under these assumptions, only considering the reaction with OH, the lifetime of NO_2 amounts to 9.7 h with a rate coefficient of 1.1×10^{-11} cm^3/s (from Sander et al. (2003) for 285 K and 1013 mbar). After 12 h, only 29% of the initial NO_2 is present. Together with the measured three times higher CHOCHO concentrations, the CHOCHO-to-NO_2 ratio would increase by a factor of 10 which is one magnitude less than the measured ratio. Thus, it appears likely that there are other processes contributing to the high CHOCHO-to-NO_2 ratio than only NO_x removal by OH. Such processes could include additional NO_x sinks, reduced CHOCHO sinks over the Gulf of Maine compared to Cambridge, or an additional CHOCHO source to the atmosphere over the Gulf of Maine. The chemistry influencing the CHOCHO-to-NO_2 ratio requires further investigation, and will be the subject of another forthcoming paper.

6 Conclusions

For the first time glyoxal (CHOCHO) could be detected by passive multi axis differential optical absorption spectroscopy (MAX-DOAS). The measurements were performed in the framework of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) 2004 campaign at MIT, Cambridge, USA, and on board the research vessel Ron Brown in the Gulf of Maine. For the retrieval, the absorption bands between 420 and 460 nm were used and optical densities of CHOCHO up to 3.5×10^{-3} could be detected. Besides the slant column densities of CHOCHO, planetary boundary layer (PBL) heights and mixing ratios in the PBL, which was assumed to be well mixed, could be retrieved for a nearly clear day at each site by means of radiative transfer modeling. Mixing ratios at MIT varied from 40 to 120 ppt while over the Gulf of Maine they were found up to three times larger than at MIT. The CHOCHO-to-NO_2 ratios showed clear diurnal cycles with maxima in the middle of the day. The ratio over the Gulf of Maine was 110±45 times higher than at MIT. NO_x removal is found to be one responsible factor for this enhancement, but also other factors seem to play a role and will be subject of a companion paper that focuses more on the chemistry involved to explain these observations.

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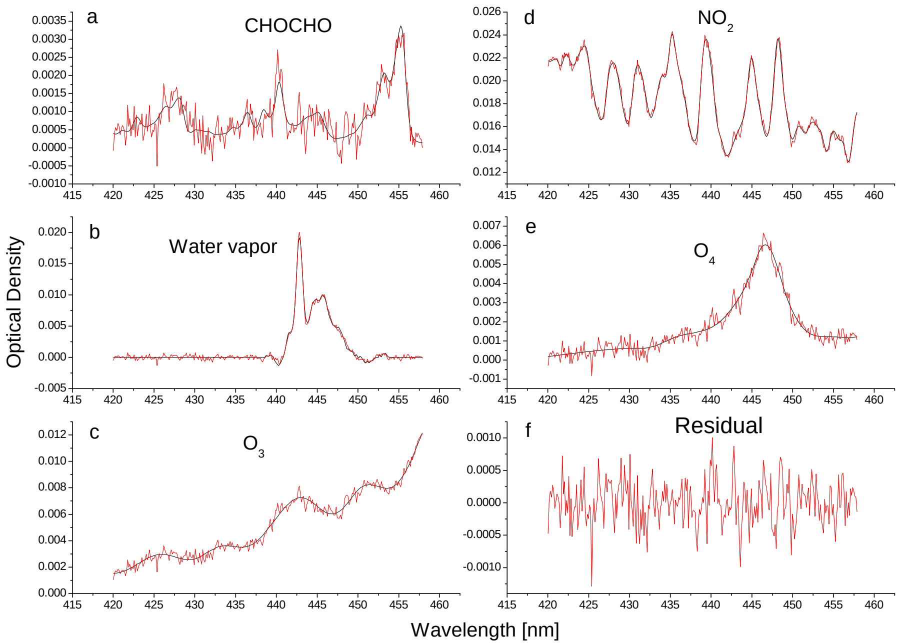

Fig. 1. CHOCHO example retrieval of a spectrum taken on 10 July 2004, 05:15 p.m. at a 3° elevation angle. The optical densities of the scaled cross-sections (black) and their added residuals (red) as a function of wavelength are plotted, **(a)** for CHOCHO, **(b)** for water vapor, **(c)** for O_3, **(d)** for NO_2 and **(e)** for O_4. **(f)** shows the residual.

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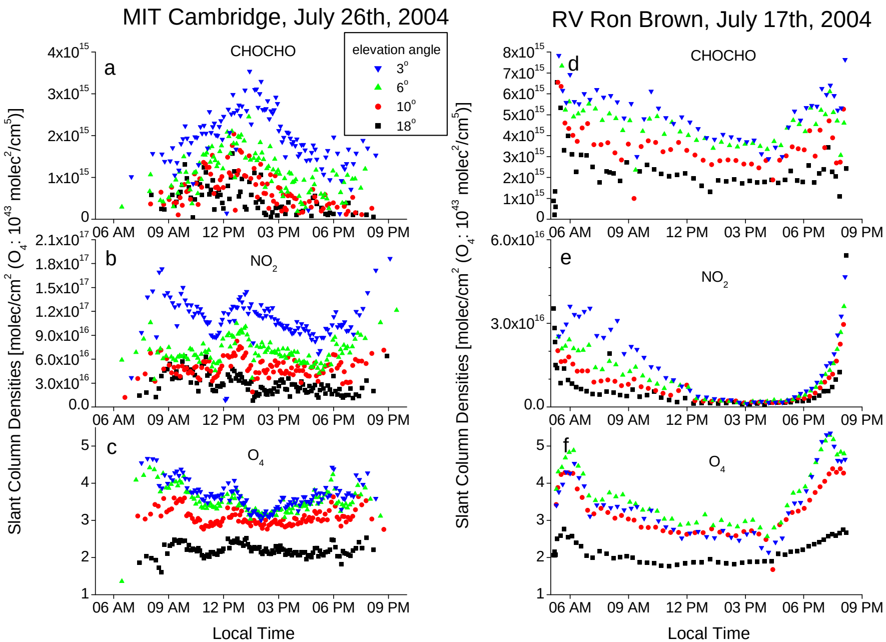

Fig. 2. SCDs of CHOCHO, NO_2 and O_4 at MIT in Cambridge on 26 July 2004 **(a)–(c)** and RV Ron Brown on 17 July 2004 **(d)–(f)**. The elevation angles are indicated by the symbol color as denoted in the legend.

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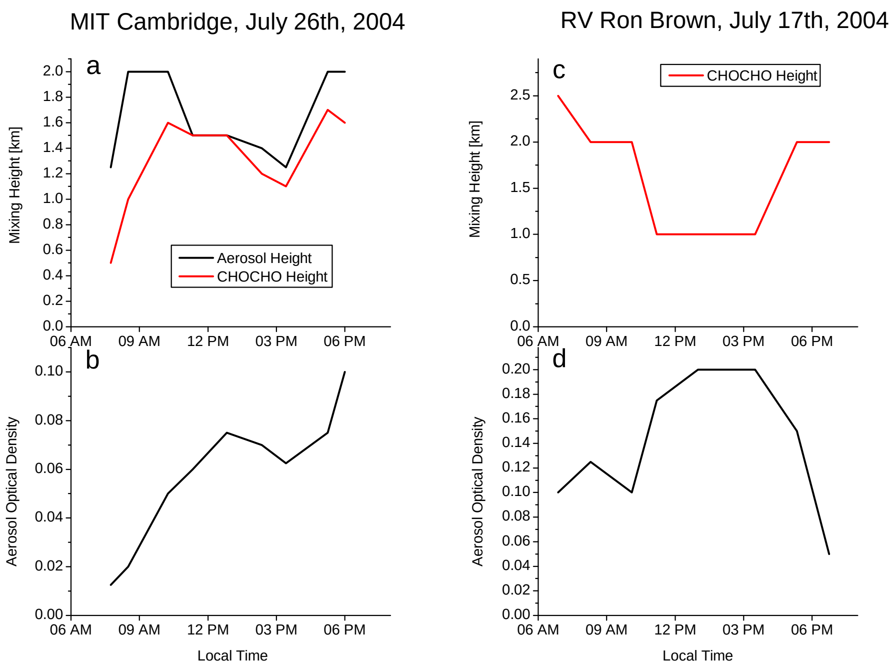

Fig. 3. Estimated mixing height for CHOCHO and aerosol (only for MIT) as well as aerosol optical density at MIT in Cambridge on 26 July 2004 (**a** and **b**) and RV Ron Brown on 17 July 2004 (**c** and **d**) retrieved by radiative transfer modeling.

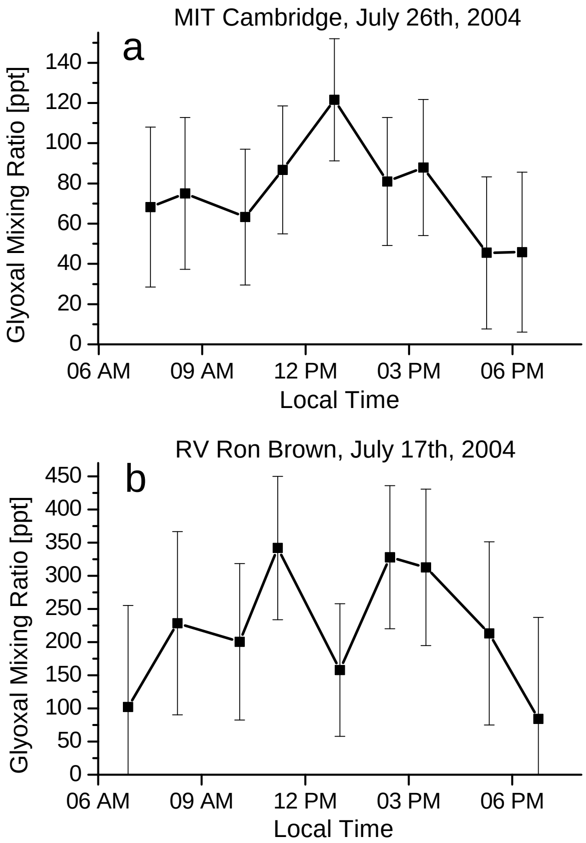

Fig. 4. CHOCHO mixing ratios at MIT in Cambridge on 26 July 2004 **(a)** and RV Ron Brown on 17 July 2004 **(b)** retrieved by radiative transfer modeling from CHOCHO SCDs.

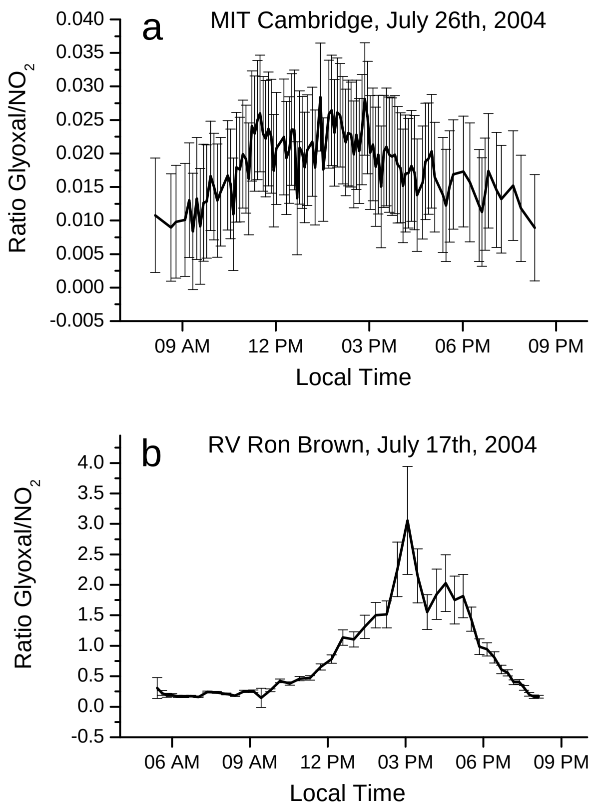

Fig. 5. CHOCHO-to-NO_2 SCD ratios of the 3° elevation values at MIT in Cambridge on 26 July 2004 **(a)** and RV Ron Brown on 17 July 2004 **(b)**.